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SAXS Study of the Surfactant-encapsulated Giant Polymolybdate Nanospheres

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Beamline(s): X10A

Introduction: The packing structures of several kinds of newly discovered polyoxomolybdate (POM) nanoclusters encapsulated by long chain surfactants (DODA, dioctadecyldimethylammonium bromide) were studied by small-angle X-ray scattering (SAXS). The surfactant-coated giant polyoxomolybdate nanoclusters can be considered as "soft spheres", which are expected to show different properties than the bare giant nanoclusters (usually referred as "hard spheres". The surfactant-encapsulated single POM giant nanoclusters have the potential applications as the nanocontainers and nanoreactors.

Methods and Materials: Small-angle X-ray scattering (SAXS) technique has been used. The giant polyoxomolybdate nanoclusters were prepared by a method reported before. The dioctadecyldimethylammonium bromide (DODA) surfactant was used to take the giant nanospheres from aqueous solution into chloroform phase. The 2D-CCD was used as the detector. The unique DSC (differential scanning calorimetry) sample cell was also used, which enabled us to monitor the temperature-dependent structure change.

Results: At room temperature, the bare POM nanoclusters formed extremely ordered primitive cubic (pc), porous structure similar to that of zeolite. Although the structure is not a closed-packing one, it is fairly firm and hard to be broken. With increasing temperature to over 370 °C, the same pc structure remained, but the size of the unit cell continuously decreased (from 5.1 nm at room temperature to below 4.0 nm). Considering that the hollow spherical POM structure is quite conservative, the change of the crystal lattice can be explained only by the fact that the POM nanoclusters lost some of their components, e.g., absorbed small molecules. The packing of the "soft balls" were totally different from that of the "hard balls", and were variable to temperature, surfactant hydrophobic chain length and the relative molar ratio of the surfactant to the nanoclusters. Detailed study on this area is on the way.

Conclusions: The SAXS equipments including the 2-D CCD camera and DSC sample cell at X10A were ideally suitable for the study of the surfactant-encapsulated giant POM nanoclusters at different temperatures. The preliminary results indicated that the crystal lattice of POM nanoclusters showed unusual and strong temperature dependence. The packing structure of the POM was changed when they were coated by surfactants. Many external parameters, e.g., temperature, surfactant chain length and the amount of surfactant, played roles in determining the packing structures of POM nanoclusters.

References: T. Liu, Q. Wan, Y. Xie, C. Burger, L.-Z. Liu, B. Chu, J. Am. Chem. Soc. 2001, web-released on Oct. 11th, in press.